

Effect of Sintering Temperature on Property of Low-Density Ceramic Proppant Adding Coal Gangue

Jiaying HAO^{1*}, Huilan HAO¹, Yunfeng GAO¹, Xianjun LI², Mei QIN¹, Kaiyue WANG¹

¹ Institute of Materials Science and Engineering, Taiyuan University of Science and Technology, Taiyuan 030024, Shanxi, China

² Department of Civil Engineering, Shanxi University, Taiyuan 030013, Shanxi, China

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Calcined flint clay (45.6 wt.% Al₂O₃) and solid waste coal gangue were used to prepare low-density ceramic proppant by solid state sintering method. The density and breakage ratio of the ceramic proppant were systematically investigated as a function of sintering temperature. The morphology and phase composition of the ceramic proppant were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results show that the ceramic proppant is composed of rod-like mullite and granular cristobalite. Bulk density and apparent density of the proppant first rise and then slightly decrease with increasing the sintering temperature, while breakage ratios under 35 MPa and 52 MPa pressure gradually decrease and then increase. As the sintering temperature increases up to 1400 °C, the ceramic proppant shows denser microstructure. The proppant sintered at 1400 °C have the best performance with 1.27 g/cm³ of bulk density, 2.79 g/cm³ of apparent density, 3.27 % of breakage ratio under 35 MPa closed pressure and 8.36 % of breakage ratio under 52 MPa closed pressure, which conform to the requirement of low-density ceramic proppant. The addition of solid waste can greatly reduce the preparation cost of the ceramic proppant.

Keywords: ceramic proppant, low-density, coal gangue, sintering.

1. INTRODUCTION

Oil fracturing proppant, used to “prop open” rock cracks, is key material in the exploration of oil and gas deep wells, and can increase the output of natural oil and gas wells [1]. Generally, the proppant with different strength and performance need to be developed according to the difference of oil and gas field. Now, quartz sand and ceramic proppant are more widely used in the hydraulic fracturing [2]. Since Stanolind Oil conducted the first experimental fracturing in the Hugoton field utilizing sand from the Arkansas River in 1947, sand has remained the most commonly used proppant for hydraulic fracturing process because of economic advantages [3]. However, the strength of quartz sand is insufficient for the long-term use of underground wells and quartz sand has poor sphericity [4]. Compared to quartz sand, ceramic proppant has more uniform in size and shape, and has higher sphericity and roundness to yield higher porosity and permeability of the proppant bed. Furthermore, ceramic proppant has superior performances, especially in terms of crush resistance [5].

Ceramic proppant can be further divided into three broad classifications based on its density: low-density ceramic, intermediate-density ceramic and high-density ceramic [6]. Low-density ceramic proppant is easy to pump and not easy to precipitate, and can reduce the viscosity requirements of the hydraulic fracturing fluid, reduce the damage to the pump, and effectively reduce the difficulty of construction and the cost of exploitation. Therefore, the ideal fracturing material should be low-density high-strength ceramic proppant [7].

The proppant density is typically governed by the percentage of alumina in the pellet, and, when the ceramic proppant is made properly, the alumina content will be proportional to the pellet strength [8]. High density of ceramic proppant currently used mainly results from the raw material of high-alumina bauxite [2]. Bauxite ore also makes the preparation cost of the ceramic proppant increase. Flint clay is also a natural ore containing Al₂O₃ and SiO₂ and its Al₂O₃ content is much lower than that of bauxite. But Al₂O₃ content can increase after flint clay is calcined. Flint clay ore is rich in China.

Coal gangue is a hazardous by-product of coal mining industry and its average production is about 10–15 % of raw coal production [9]. Efficient disposal of coal gangue is a worldwide problem owing to its massive accumulation and harmful effects on the environment [10]. Statistics show that approximately 3000 hills of coal gangue exist in China, the stockpile of coal gangue has reached 4.6–5.0 billion tons, and 0.2 billion tons of coal gangue is produced annually [11]. The huge amount of reserve is also a most important economic concern owing to the low utilization. Therefore the utilization of coal gangue has attracted extensive interests in recent years [12]. Efforts have been made to use coal gangue for different purposes. For example, coal gangue has been used in the manufacture of building products (pottery, cement, etc.) and refractories (mullite, SiC, etc.) [13]

Coal gangue has various chemical and mineral compositions and generally contains certain content of SiO₂ and Al₂O₃, [14] which are necessary ingredients for preparing ceramic proppant. Other components in coal

* Corresponding author. Tel.: +86-351-2306774.
E-mail address: jty2280@163.com (J. Hao)

gangue can help to decrease the sintering temperature. Therefore, cheap flint clay and solid waste coal gangue can replace bauxite as raw materials of ceramic proppant.

In this research, low-cost low-density ceramic proppant was successfully prepared by raw materials of calcined flint clay partially replaced by coal gangue. Furthermore, the dependence of phase evolution, microstructure, bulk density, apparent density and breakage ratio on sintering temperature was thoroughly investigated.

2. EXPERIMENTAL DETAILS

Natural flint clay and solid waste coal gangue (Shanxi Yangquan, China) were used as raw materials. In order to ensure the alumina content in flint clay, flint clay was calcined at 1200 °C for 1 h using a muffle furnace. The chemical composition of the calcined flint clay was measured according to the Chinese Nonferrous Metals Industry Standard (YS/T 575-2007) and that of coal gangue was measured on the basis of the National Standard of PRC (GB/T 27974-2011). The tested results are displayed in Table 1. The phase analysis of the raw materials is presented in Fig. 1.

Table 1. Chemical compositions of the raw materials (wt.%)

	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	L.O.I
Burnt flint clay	45.6	37.8	1.13	2.6	0.47	12.4
Coal gangue	36.29	45.75	3.29	1.02	0.32	13.33

The proppant was prepared by pelleting, drying, screening and sintering, namely solid state sintering method. The weight ratio of coal gangue with respect to the calcined flint clay was 1 to 4. First, the raw materials were mixed homogeneously in a strong mixing machine (R02, Eirich Co. Ltd, Germany) followed by formation of spherical green bodies with the addition of water. Second, after drying at 100 °C for 2 h in a drying box (DH-101-2BS, Tianjin central experiment Furnace Co. Ltd, China), the green proppant was passed through a set of sieves of 20/40 meshes (aperture size of 0.85–0.43 mm). Then the 20/40 mesh proppant particles were placed in a cylindrical corundum crucible and sintered in a high temperature box-type sintering furnace (KBF1700, Nanjing Bo Yun Tong Instrument Technology Co. Ltd, China) at different temperatures (1250 °C, 1300 °C, 1350 °C, 1400 °C and 1450 °C, respectively) in air for 2 h at a heating rate of 5 °C/min. Finally, the proppant was cooled at a cooling rate of 5 °C/min by furnace cooling. The cooled ceramic proppant was passed through the sieves of 20/40 meshes.

The phase compositions of the ceramic proppant were identified by powder X-ray diffraction (XRD, X'Pert PRO; Philips Co. Ltd, Holland) utilizing Ni filtered Cu K α radiation with operating voltage of 40 kV, scanning range of 20°–80°, scanning speed of 20°/min and scanning step 0.02°. The microstructures of the sample were examined by a field emission scanning electron microscope (FESEM, S-4800; Hitachi, Japan) with operating voltage of 10 kV and magnification of ten thousand times.

Bulk density and apparent density of the ceramic proppant were measured by a density bottle. First, weigh

the 25 mL density bottle. Then the proppant were loaded into the density bottle until the 25 mL scale. Do not shake and weigh the mass. Repeat three times to take the average. The bulk density was the net weight of the proppant.

The apparent density was calculated as follows. First, fill the bottle with water and weigh it, and calculate the volume of the water (V_1). Second, pour out the water from the bottle and dry it. Add a certain amount of proppant into the bottle and weigh. Then fill the bottle with water, remove the bubbles, and continue to fill water and weigh. The volume of the proppant can be calculated by V_1 minus the volume of water in the bottle with the proppant. The apparent density was calculated by dividing the mass of the proppant by the volume of the proppant. Repeat three times to take the average.

According to the Chinese Petroleum and Gas Industry Standard (SY/T5108-2014), the breakage ratio is calculated by the formula:

$$\eta = \omega_c / \omega_0 \times 100\%, \quad (1)$$

where ω_c and ω_0 are respectively the weight of crushed specimen after and before testing. Breakage ratio was tested under 35 MPa and 52 MPa closed pressure.

3. RESULTS AND DISCUSSION

The XRD patterns of the raw materials (calcined flint clay and coal gangue) are shown in Fig. 1. From Fig. 1 a, the main phase of calcined flint clay is donbassite, kaolinite, CaAl₈Fe₄O₁₉ and Ca-Al-Si-O, while it can be found in Fig. 1 b that coal gangue mainly contains quartz, kaolinite, muscovite and dolomite.

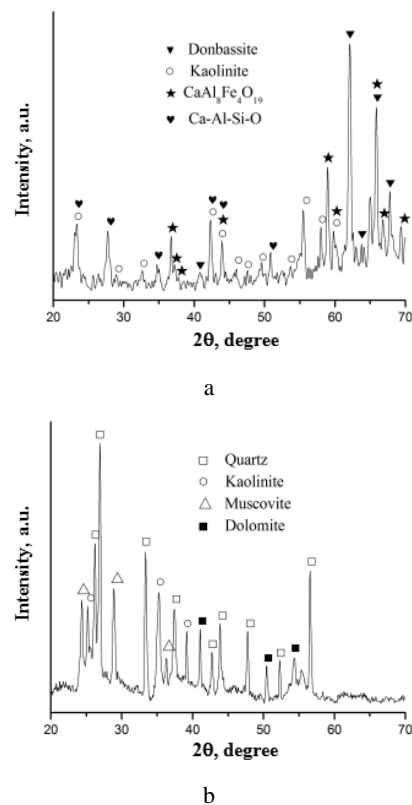


Fig. 1. XRD patterns of the raw materials: a – calcined flint clay; b – coal gangue

The XRD patterns of the ceramic proppant sintered at 1250 °C–1450 °C for 2 h are presented in Fig. 2. It can be seen that the main crystalline phases of the ceramic proppant are mullite (JCPDS: 15-0776) and cristobalite (JCPDS: 27-0605). Also planes and d-spacings of the mullite crystal are listed in Table 2. The two diffraction peaks of 2 θ at 21.604° and 35.626° in Fig. 2 correspond to cristobalite planes (111) and (220) with d-spacings of 4.1100 nm and 2.5180 nm, respectively. Mullite results from the reaction of Al₂O₃ and SiO₂, and cristobalite is formed from the transformation of SiO₂. From the patterns, when the sample is sintered at 1250 °C, the diffraction peaks of mullite phase are obvious and sharp, which indicates solid phase reaction at low temperature has proceeded. With the increase of sintering temperature, the diffraction peaks of mullite phase gradually become stronger. This declares the formation reaction of mullite is relatively complete. However, the diffraction peak intensity of cristobalite phase apparently decreases with the rise of sintering temperature. The diffraction peak intensity of cristobalite phase is the minimum when the ceramic proppant is sintered at 1400 °C. Subsequently, the diffraction peak intensity of cristobalite phase increases again, and reaches the maximum at 1450 °C. This indicates that the solid phase reaction has been carried out with the increase of sintering temperature.

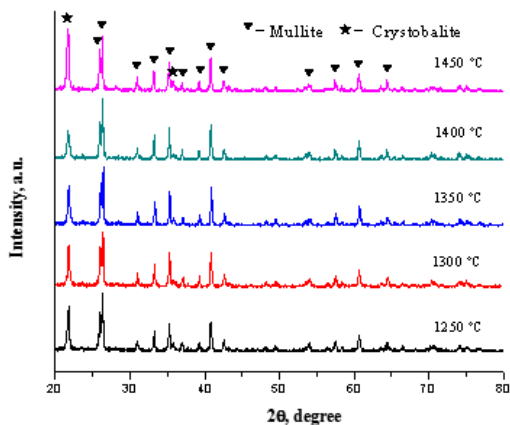


Fig. 2. XRD patterns of the ceramic proppant sintered at different temperatures

Table 2. Planes and d-spacings of the mullite crystal

2 θ , degree	(h k l)	d-spacing, nm	2 θ , degree	(h k l)	d-spacing, nm
25.971	(1 2 0)	3.4280	40.874	(1 2 1)	2.2060
26.267	(2 1 0)	3.3900	42.590	(2 3 0)	2.1210
30.960	(0 0 1)	2.8860	53.883	(3 2 1)	1.7001
33.228	(2 2 0)	2.6940	57.561	(0 4 1)	1.5999
35.278	(1 1 1)	2.5420	60.711	(3 3 1)	1.5242
36.993	(1 3 0)	2.4280	64.571	(0 0 2)	1.4421
39.276	(2 0 1)	2.2920			

Fig. 3 presents SEM images of the ceramic proppant sintered at different temperatures. From Fig. 3 a there exist more granular particles, which represent mullite and cristobalite crystals. This is because the crystal is not fully grown up at the lower sintering temperature. In addition, there are some very short rod-like mullite crystals with the

diameter of about 300 nm and the length of about 1 μ m, and big pores with the diameter of 1.5 μ m in the structure. These pores are connected and belong to open pores. When the ceramic proppant is sintered at 1300 °C (Fig. 3 b), short rod-like mullite crystals begin to develop, and big pores with the diameter of about 1 μ m still exist. The ceramic proppant obtained at 1350 °C show more rod-like mullite grains (Fig. 3 c), and granular cristobalite grains disperse in mullite grains. Big pores disappear and the structure is compact. When the sintering temperature is up to 1400 °C (Fig. 3 d), the rod-like mullite grains obviously grow up. The diameter is between 200 nm and 400 nm, and the length is in the range of 500 nm and 3 μ m. There is a closed pore with the diameter of about 1.5 μ m in the structure. In addition, the boundaries between the rod-like mullite grains begin to become obscure, which is mainly due to the glass phase generated at high temperature. Furthermore, several granular cristobalite particles are scattered around the mullite phases. In Fig. 3 e, the more glass phase generated at high temperature make the mullite and cristobalite grains compactly stick together. In comparison, the ceramic proppant sintered above 1400 °C possess more compact structure than those sintered at below 1400 °C, which could be attributed to the excess glass phase.

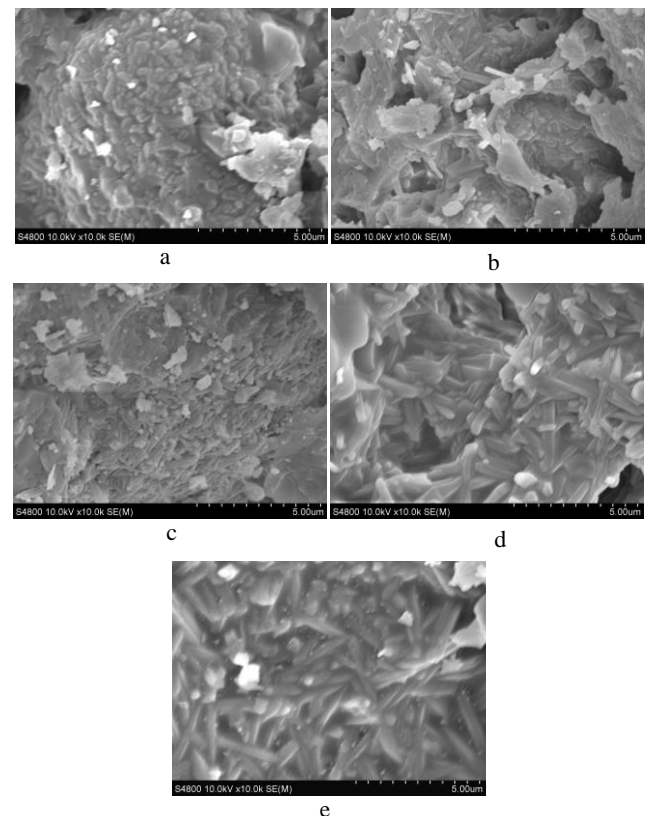


Fig. 3. SEM images of the ceramic proppant sintered at: a – 1250 °C; b – 1300 °C; c – 1350 °C; d – 1400 °C; e – 1450 °C

Bulk density and apparent density of the prepared ceramic proppant are shown in Fig. 4. It is obvious that the both densities present an increasing trend with the increase of sintering temperature. However, bulk density and apparent density of the ceramic proppant decrease slowly when the sintering temperature is up to 1400 °C. It is

known from the above SEM results that there are many pores in the microstructure of the ceramic proppant sintered at lower temperature. Therefore, bulk density and apparent density are lower at low temperature. Subsequently, the structures of the ceramic proppant become compact as the sintering temperature rises, which can make the density increase. When the sintering temperature rises to 1400 °C, the both densities reach the maximum value. This can be attributed to glass phase generated with increasing temperature. The increase of sintering temperature accelerates the reaction rate, which is beneficial to the exclusion of pores and the shrinkage of volume, thereby promoting the densification of the ceramic proppant. Bulk density and apparent density of the prepared ceramic proppant is respectively 1.27 g/cm³ and 2.79 g/cm³ when sintering temperature is up to 1400 °C, which conform to the requirements of low-density ceramic proppant. Furthermore, bulk density of the ceramic proppant sintered at 1450 °C is almost unchanged, while apparent density slightly decreases.

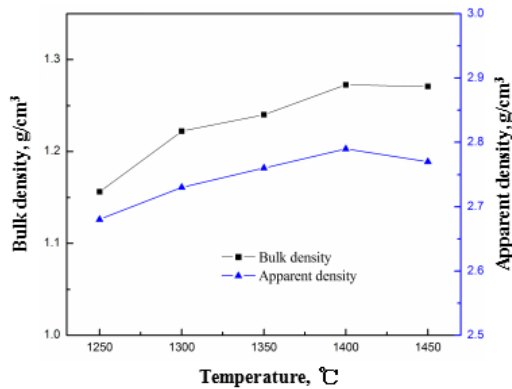
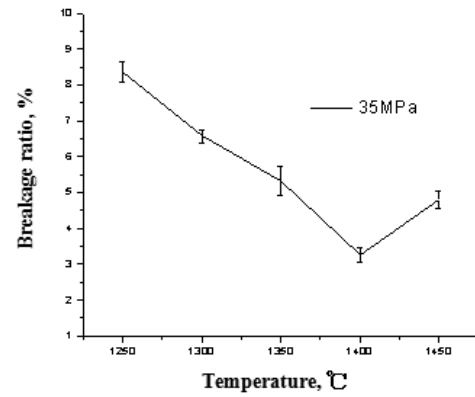
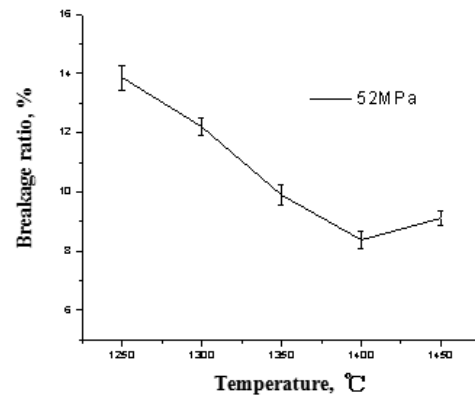


Fig. 4. Bulk density and apparent density of the ceramic proppant sintered at different temperatures

Fig. 5 are breakage ratio of the ceramic proppant sintered at different temperatures under 35 MPa and 52 MPa closed pressure. As is seen in Fig. 5, breakage ratios of the proppant first decrease and then increase with the increase of sintering temperature. Breakage ratios of the ceramic proppant under 35 MPa and 52 MPa are the minimum value as the sintering temperature is up to 1400 °C, respectively 3.27 % and 8.36 %, which meet China industrial standard requirements SY/T 5108-2014. This is ascribed to the high compactness of ceramic proppant as mentioned above. With the elevation of sintering temperature, more mullite grains formed can make the strength of ceramic proppant increase, because mullite plays a toughening role in the structure [15]. But above all, the glass phase resulted at high temperature can perform the bonding effect on the crystalline grains. The further increase of sintering temperature make the breakage ratios of the proppant slightly decrease. This is consistent with the results of the above. However, it is the most important that the addition of solid waste coal gangue greatly reduces the preparation cost of ceramic proppant.



a



b

Fig. 5. Breakage ratio of the ceramic proppant under: a–35 MPa pressure; b–52 MPa pressure

4. CONCLUSIONS

Low-density ceramic proppant was successfully prepared from flint clay and solid waste coal gangue. The prepared ceramic proppant is mainly composed of rod-like mullite and granular cristobalite. Compared with the proppant prepared from bauxite, the proppant prepared from calcined flint clay and solid waste coal gangue shows the lower density. Bulk density and apparent density of the proppant sintered at 1400 °C is respectively 1.27 g/cm³ and 2.79 g/cm³, and the lowest breakage ratio under 35 MPa and 52 MPa closed pressure are respectively 3.27 % and 8.36 %. The low-density ceramic proppant meets the requirements of the ideal fracturing materials. In addition, the addition of coal gangue greatly reduces the preparation cost of ceramic proppant, meanwhile develops a new way of solid waste recycling. Therefore, it is feasible to prepare the ceramic proppant using flint clay and coal gangue. The ceramic proppant will become desired candidate for fracturing proppant in future applications.

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